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Journal of Hazardous Materials 148 (2007) 47–55
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Hybrid biosorbent: An innovative matrix to enhance the biosorption of Cd(II) from aqueous solution

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Received 19 November 2006; received in revised form 4 February 2007; accepted 5 February 2007
Available online 11 February 2007

Abstract

To enhance the metal removing capacity of a fungus biosorbent, a new idea of producing a hybrid biosorbent (HB) matrix by combining two different biosorbents using a simple and low-cost immobilization technique was tested for the sorption of Cd(II). The two biosorbents, used as the building block for the production of HB matrix, were the fungal biomass of *Phanerochaete chrysosporium* (B1) and fibrous network of papaya wood (B2). Maximum independent biosorption capacity of B1 and B2 was noted, respectively, to be 71.36 and 17.62 mg Cd(II) g^{-1} biosorbent. However, when two biosorbents were hybridized to form HB matrix, the combined biosorption capacity (141.63 mg Cd(II) g^{-1} biosorbent) was increased by 98.47, 703.80%, respectively, as compared to the ability of B1 and B2 when used alone, and by 59.17% than the sum of separate individual abilities of biosorbents B1 and B2. The kinetics of equilibrium was fast, approximately 88% of Cd(II) biosorption taking place within 30 min. Biosorption kinetics and equilibria followed the pseudo-second order kinetics and Langmuir adsorption isotherms model. HB matrix was also shown to be highly effective in removing Cd(II) from aqueous solution in a continuous flow fixed-bed column bioreactor, both in batch and repeated cycles.

Keywords: Hybrid biosorbent; Metal biosorption; *Phanerochaete chrysosporium*; Papaya wood; *Carica papaya*; Cd(II) removal

1. Introduction

Cd(II) is among the most toxic metals and is known to cause renal dysfunction, bone degeneration, lung insufficiency, liver damage and hypertension in humans [1]. On the basis of these adverse health effects, Cd(II) has been included in the red list of priority pollutants by the Department of Environment, UK [2] and in the black list of EEC dangerous substances directive [3]. US Environment Protection Agency has also classified Cd(II) as Group B1 carcinogen [4].

The major sources of Cd(II) release into the environment through wastewater streams are electroplating, smelting, alloy and plastic manufacturing, pigments, battery, fertilizers, mining and metal refining processes [5]. The most commonly used procedures for the treatment of Cd(II) containing effluents include chemical precipitation, evaporation, ion exchange and membrane separation. Techno-economic considerations, however, limit their wide-scale applications [6]. Therefore, the need for the development of economical, effective and safe methods for Cd(II) removal has led to the search for alternative procedures.

The use of biological materials in general and fungi in particular has received considerable attention during recent decades for the removal of heavy metals as the environment friendly alternative technology [7]. Many fungal species, such as *Aspergillus niger* [8], *Mucor rouxii* [9], *Phanerochaete chrysosporium* [10], *Phomopsis* sp. [11], *Polyporus versicolor* [12], *Rhizopus arrhizus* [13] and *Trametes versicolor* [14] have been tested and the metal biosorption capacities for most of these fungal biomass were found very attractive. The application of these fungal biosorbents on a commercial scale, however, has been hindered by operational limitations associated with their physical characteristics, such as small particle size with low density, poor mechanical strength and low rigidity, and solid–liquid separation [15].

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doi:10.1016/j.jhazmat.2007.02.009

As an alternative, a number of agro-based plant waste materials, such as coconut fibres [16], black gram husk [17], fibrous network of papaya wood [18], petiolar felt-sheath of palm [19] and rice husk [20] have been tested as a low-cost metal biosorbents. The adsorption capacity of these agro-based plant waste materials is, however, generally low which in practical terms means their use in large volumes, rendering their application impractical. To overcome the problems associated with the application of both microbial and agro-based materials as the biosorbent, a novel idea of producing a hybrid biosorbent (HB) was considered and an innovative HB matrix was produced by combining two previously known biosorbents, namely, the hyphal biomass of *P. chrysosporium* (B1) and the fibrous network of papaya wood (B2) using a simple technique of immobilization [21] in which two known metal sorbents act as complementing partners.

Application of this HB matrix is reported here as an innovative, inexpensive and environment-friendly biosorbent, for the first time, for the removal of Cd(II) from aqueous solution. Attempts were also made to characterize the various biosorption process parameters (i.e. pH, equilibrium time, initial metal ion and biosorbent concentration and adsorption isotherm modelling) influencing the metal adsorption–desorption in anticipation of the potential use of this newly developed immobilized biosorption system to large scale metal recovery systems in near future. To highlight the importance of HB matrix, a comparison was drawn between the biosorption capacity of HB matrix and the biosorption capacity of free biomass of *P. chrysosporium* (B1) and the structural fibrous network of papaya wood (B2) when used singly, and with other biosorbents reported earlier in literature.

The selection of white rot fungi *P. chrysosporium* (B1), was made due to its reported metal biosorption capacity [22] and also its versatile ability to degrade a wide variety of environmentally hazardous compounds like polycyclic aromatic hydrocarbons [23], chlorinated organics [24] and synthetic dyes [25] whereas fibrous network of papaya wood [B2], an agro-based plant material used to entrap B1, was chosen due to its previously reported metal biosorption potential [18], low cost and highly porous structural network, prerequisite for stable microbial entrapment.

2. Materials and methods

2.1. Microorganism and culture medium

P. chrysosporium (ATTC 24725) was maintained by subculturing on potato dextrose agar slants. Hyphal suspension for immobilization was prepared from 7-day old cultures grown on potato dextrose agar plates at $35 \pm 2\,^{\circ}C$. The liquid growth medium consisted of ($g\,l^{-1}$ of distilled water; pH adjusted to 4.5): D-glucose, 10.0; KH_2PO_4, 2.0; $MgSO_4.7H_2O$, 0.5; NH_4Cl, 0.1; $CaCl_2.H_2O$, 0.1; thiamine, 0.001.

2.2. Preparation of HB matrix

Fibrous network of papaya wood (B2) was obtained from the felled dried trunk of the matured tree of *Carica papaya*. The trunk, 15–20 cm diameter, appears like a hollow collapsible cylinder. The cylinder wall, 0.5–0.8 cm thick, is a weak woody structure, made up of intertwining fibrous tissue mass. The outer wood surface is covered by papery bark, which on peeling exposes a honey beehive like structure (Fig. 1), constructed by several fibrous bundles meshed together in easily peelable layers. To obtain the fibrous network of papaya wood, the hollow cylindrical papaya trunk was cut into small pieces (2 cm × 2 cm), soaked in boiling water for 30 min, thoroughly washed under tap water and left for 2–3 h in distilled water, changed three to four times. The washed wood pieces were oven dried at 80 °C to constant weight, autoclaved for 15 min at 120 °C at 1.06 kg cm^{-1} pressure and soaked in culture medium for 5–10 min under aseptic conditions. Four preweighed wood pieces (B2) were transferred to 100 ml growth medium contained in 250 ml Erlenmeyer flasks. Each of these flasks was inoculated with 0.5 ± 0.024 ml of fungal mycelium suspension (B1) and incubated at 35 °C and shaken at 100 rpm for 6 days. The fungal mycelium suspension, optical density 0.5 ± 0.021 at 650 nm, was prepared from stationary phase culture of *P. chrysosporium*. After five days, *P. chrysosporium* biomass (B1) was found entrapped within the fibrous network of papaya wood (B2) to form a hybrid biosorbent (HB) matrix. The HB matrix so produced was harvested at the day 6 of incubation (Fig. 1), washed twice with distilled water and stored at 4 °C until use. The dry weight of the B1 within B2 was determined as the weight difference of B2 before and after entrapment of B1 dried at 70 °C overnight. For scanning electron microscopy, samples were coated with a thin layer of gold under vacuum and examined using a Philips PSEM 501B Scanning Electron Microscope.

2.3. Biosorption studies

The biosorption of Cd(II) by HB matrix from aqueous solution was carried out in batch biosorption-equilibrium studies. Desired concentrations of Cd(II) solutions were prepared by diluting 1000 ± 2 mg l^{-1} standard Cd(II) stock solution [$Cd(NO_3)_2$, Merck Ltd., Poole, UK]. pH of the solution was adjusted to 5.0, using 0.1 M NaOH. Fresh dilutions were used for each biosorption study. The biosorption capacity of B1, B2 and HB matrix (100 mg) was determined by contacting 100 ml Cd(II) solutions of known concentrations (10–500 mg l^{-1}) in 250 ml Erlenmeyer flasks. The Cd(II) solution, incubated with the HB matrix, was shaken on an orbital shaker at 100 rpm in tightly stopper flasks at $25 \pm 2\,^{\circ}C$. B1 was removed from metal solution by centrifugation at 5000 rpm for 5 min, whereas B2 and HB matrix were separated from the solution by simple decantation. Residual concentration of Cd(II) in the metal supernatant solutions was determined using atomic absorption spectrophotometer (UNICAM-969, Unicam Cambridge, UK, operated with software "Solaar 32". Fuel (air–acetylene) flow rate was set at 1.3 l min^{-1}. The working current/wavelength for Cd(II) ions was 8.0 mA/228.8 nm.. Deuterium background correction was applied and standard solutions of five different concentrations were used for calibration. A quality control standard was inserted after every 15 samples.

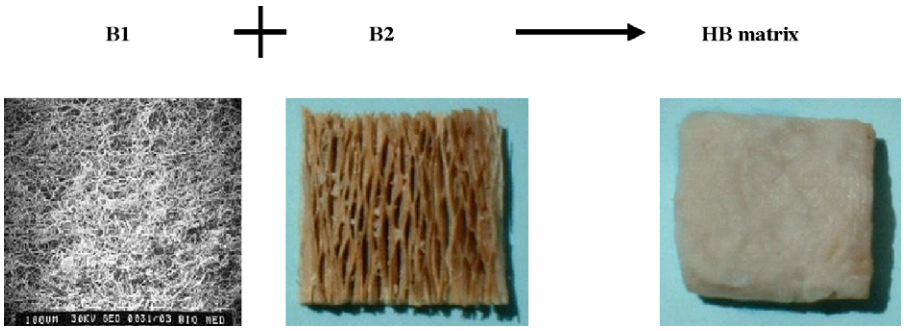

Fig. 1. Hyphal biomass of *Phanerochaete chrysosporium* (B1), fibrous network of papaya wood (B2) and hybrid biosorbent (HB) matrix produced by immobilizing *P. chrysosporium* on papaya wood.

2.4. Biosorption isotherms modelling

The Langmuir and Freundlich equilibrium models [26,27] were used for the evaluation of adsorption data. The Langmuir model assumes monolayer adsorption which is expressed as:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + bC_{eq}} \quad (1)$$

where q_{eq} and q_{max} are the equilibrium and maximum uptake capacities (mg metal g^{-1} biosorbent), C_{eq} the equilibrium concentration (mg metal l^{-1} solution) and b is the equilibrium constant ($l\,mg^{-1}$). The Langmuir equation can be experimentally tested by plotting C_{eq}/q_{eq} against C_{eq}; a straight line confirms that the adsorption isotherm validly fits the Langmuir model.

The Freundlich model is presented as follows:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

where K_F and n are Freundlich constants of the system. The Freundlich equation can be tested by plotting $\log q_{eq}$ against $\log C_{eq}$; a straight line confirms that the adsorption isotherm validly fits the Freundlich model.

2.5. Biosorption kinetics modelling

In order to examine the controlling mechanism of biosorption process, such as mass transfer and chemical reaction, the pseudo-first order and the pseudo-second order kinetic models, were used to test the experimental data of Cd(II) biosorption by HB. The first order rate equation of the Lagergren [28] is represented as:

$$\ln(q_{eq} - q_t) = \ln q_{eq} - K_{1ad} t \quad (3)$$

where q_{eq} (mg metal g^{-1} biosorbent) is the mass of metal adsorbed at equilibrium, q_t (mg metal g^{-1} biosorbent) the mass of metal adsorbed at time t and K_{1ad} (min^{-1}) is the first order reaction rate equilibrium constant. The pseudo-first order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. A straight line of $\ln(q_e - q_t)$ versus t indicates the application of the first order kinetics model. In a true first order process, $\ln q_{eq}$ should be equal to the intercept of a plot of $\ln(q_{eq} - q_t)$ against t.

The pseudo-second order equation [29] based on adsorption equilibrium capacity may be expressed in the form:

$$\frac{t}{q_t} = \frac{1}{K_{2ad} q_{eq}^2} + \frac{t}{q_{eq}} \quad (4)$$

where K_{2ad} (g mg^{-1} min^{-1}) is the second order reaction rate equilibrium constant. A plot of t/q_t against t should give a linear relation ship for the applicability of the second order kinetics.

2.6. Continuous removal of Cd(II) by HB packed in fixed-bed column bioreactor

To demonstrate the biosorption potential of HB in a continuous flow system, HB (2.04 ± 0.11 g of fungal biomass entrapped on papaya wood) was packed in an up-flow fixed-bed column bioreactor (Fig. 2). Cd(II) solution (10 mg l^{-1}, pH 5.0) was then pumped upwards through the column at a flow rate of 5 ml min^{-1}. Samples were collected at regular intervals from the effluent to measure residual Cd(II) concentrations. As the bed was saturated, the Cd(II) loading was terminated and the bed was eluted with 50 mM HCl solution to recover the loaded Cd(II) ions. The regenerated bed was washed thoroughly with deionized water before use in the next adsorption cycle.

2.7. Data reproducibility and statistical analysis

The data reported here are the mean values of three separate experiments. Statistical analysis of the data was carried out using the Duncan's multiple range test [30].

3. Results and discussion

3.1. Biosorption performance of HB matrix

Biosorption performance of the HB matrix as a function of time is shown in Fig. 3. The biosorption capacity of B1 and B2 has also been included in Fig. 3 for comparative purpose. Rapid Cd(II) biosorption rates were observed during the first 30 min of contact with HB matrix; 88.86% of the total metal was adsorbed by the HB matrix, compared with 69.56% by B1 and 55.31% by B2 individually. Biosorption equilibrium, however, was achieved by all the three biosorbents at about 60 min with

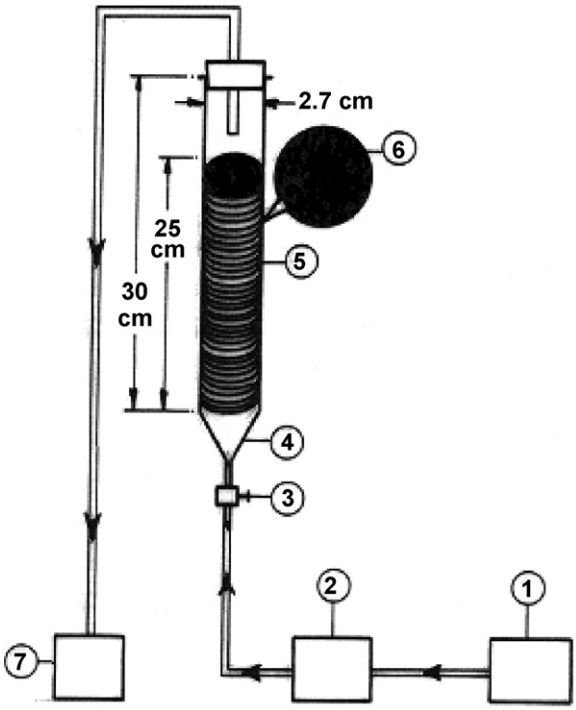

Fig. 2. Schematic diagram of fixed-bed column reactor, packed with HB designed to function as a continuous flow system for biosorption of Cd(II). 1, Metal solution reservoir; 2, peristaltic pump; 3, flow control; 4, glass column reactor; 5, HB biosorbent; 6, enlarged view of column packing; 7, effluent storage.

the maximum uptake of 46.73, 12.19 and 91.86 mg Cd(II) g^{-1} for B1, B2 and HB matrix, respectively, from 100 mg l^{-1} Cd(II) solution. The rapid rate of metal uptake by HB may be argued due to the surface immobilization of fungal hyphae (B1) on the highly porous matrix of papaya wood (B2, Fig. 1), which not only increased exposed surface area of fungal hyphae but also provide easy and quick access to heavy metal ions to the binging sites on the fungal biomass.

The statistically significant lower uptake of Cd(II) by B1 may be attributed to aggregation of the free hyphae into pellets reducing the surface area for sorption. Metal sorption efficiency of fungal hyphae has also been reported to decrease with a reduction in distance between the hyphae [31]. The rapid rate of metal sorption by HB has practical importance for applications in small reactor volumes, thus ensuring efficiency and economy. This is also a significant advantage over the other previously reported foam and gel-immobilized biosorbent systems where a significant decrease in the rate of metal uptake has been reported in comparison with free biomass [32–34]. The slower metal adsorption rate of these foam/gel-immobilized biosorbents may be attributed to the restrictions encountered by the solute to diffuse through the foam/gel membrane for reaching the functional groups on the biomass surface [31,32].

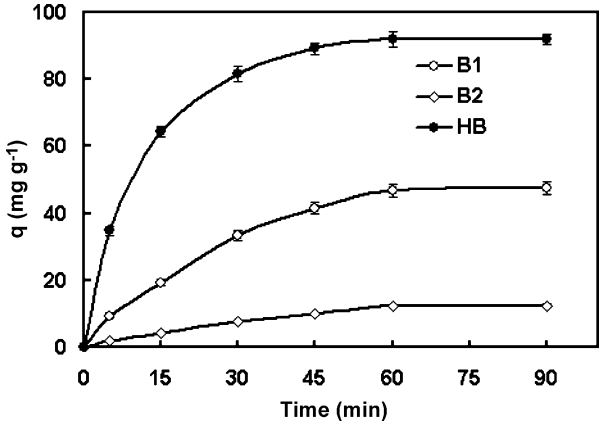

Fig. 3. Biosorption of Cd(II) from 100 mg l^{-1} solutions, pH 5.0, by hyphal biomass of *Phanerochaete chrysosporium* (B1), fibrous network of papaya wood (B2) and hybrid biosorbent (HB) matrix produced by immobilizing *P. chrysosporium* on papaya wood as related to time of contact.

3.2. Effect of pH

It has been well recognized that pH has a significant effect on the biosorption capacity of heavy metals [22]. pH affects both the solubility of metal ions and the ionization state of functional groups (carboxylic, phosphate and amino groups) on fungal cell walls [35]. In order to establish the effect of pH on biosorption of Cd(II) ions onto the B1, B2 and HB matrix, the batch equilibrium studies at different pH values were conducted in the range of 2.0–8.0. Appropriate pH of the sorption mixture was controlled by accordingly adding 0.1 M NaOH or HCl and measured at biosorption equilibrium. As can be noted in Fig. 4, the maximum sorption of Cd(II) ions on B1, B2 and HB matrix were observed at pH 6.0, which decreased significantly on reducing the pH values to 2.0.

Biosorption of Cd(II) by other immobilized and free biosorbent systems has also been reported by other researchers to be negligible at low pH values but sharp increase was shown when the pH increased from 3 to 5 [36]. The low Cd(II) biosorption capacity at pH values below 3.0 may be attributed to hydrogen ions that compete with metal ions on the sorption sites [37]. This means that at higher hydrogen ions concentrations, the biosorbent surface becomes more positively charged, thus reducing

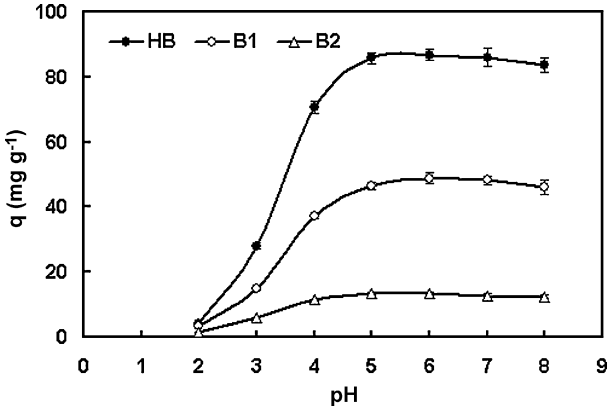

Fig. 4. Effect of pH on the biosorption of Cd(II) by *Phanerochaete chrysosporium* hyphal biomass (B1), fibrous network of papaya wood (B2) and hybrid biosorbent (HB) matrix; concentration of biosorbents = 1.0 g l^{-1}, Cd(II) concentration = 100 mg l^{-1}, controls = 100 mg l^{-1} Cd(II) solutions without any biosorbent at pH 2–8 incubated under similar conditions as were used for B1, B2 and HB matrix.

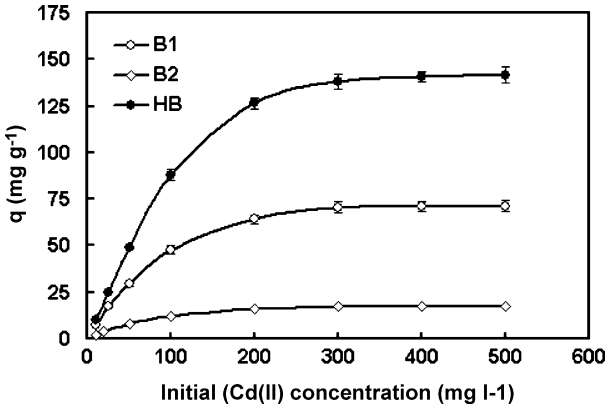

Fig. 5. Effect of initial metal ion concentration on biosorption of Cd(II) by *Phanerochaete chrysosporium* hyphal biomass (B1), fibrous network of papaya wood (B2) and hybrid biosorbent (HB) matrix; concentration of biosorbents = 1.0 g l^{-1}, pH 5.0.

the attraction between biosorbent and metal ions. In contrast, as the pH increases, more negatively charged surfaces become available thus facilitating greater metal uptake [38].

3.3. Metal removal capacity of HB matrix

Maximum metal sorption capacity of HB matrix was investigated by contacting the biosorbent with varying concentrations (10–500 mg l^{-1}) of Cd(II). Increase in the Cd(II) uptake was noted with an increase in metal ions concentration in the solution until it reached the maximum capacity of 141.63 mg Cd(II) g^{-1} biosorbent (Fig. 5). To examine the reproducibility of this unique hybrid biosorbent, the HB matrix produced in different batches were used. Excellent reproducibility of Cd(II) removal capacity was noted for the HB matrix produced in different batches of cultivation, with the maximum relative standard deviation (R.S.D.) represented as 2.39% (Table 1). This indicates that the HB matrix produced in different batches were relatively homogenous and the Cd(II) removing capacity of HB under the conditions investigated was reproducible.

Maximum Cd(II) removal capacity of HB matrix observed during the present studies (141.63 Cd(II) mg g^{-1} biosorbent) is not only 98.47 and 59.17% higher, as compared to the ability of fungal biomass (B1) when used alone, and the sum of separate individual abilities of biosorbents B1 and B2, respectively, but is also higher than those reported earlier for the removal of Cd(II) by other immobilized or free microbial biomass (Table 2). The biosorption capacity of HB matrix for Cd(II) was also compared with the commercial ion exchange resins and was noted to be significantly higher than Dowex 50 W and Doulite GT-73, and approximately equal to Amberlite IRC-718. However, HB matrix it was found to have lower sorption capacity than Amberlite 200 (Table 2). It is significant to mention that ion exchange resins are very expensive. Therefore, considering the low cost of HB matrix, simplicity of immobilization technique for the production of HB matrix, and its high metal biosorption potential, this unique biosorbent offers very attractive prospects and could thus be used for the treatment of wastewater containing heavy metals. The removal of Cd(II) by B2 was found to be 17.62 mg g^{-1}. Though it was not possible to predict how much of it contributed to the 141.63 mg g^{-1} Cd(II) biosorbed by HB matrix, yet most of it is likely to have been adsorbed on the expanded surface area of this unique biosorbent provided by the fungal hyphae biomass immobilized (B1) along the outer surface of the fibres of B2. From these results, nevertheless, it is clear that the use of B2 as an immobilization matrix for B1 has significantly enhanced the biosorption capacity of the HB matrix and has cause no negative effect on the biosorption process. This is a significant advantage over currently reported gel-immobilized alga and fungal biosorbent systems where a significant decrease in the metal removing capacity has been reported in comparison of free microbial biomass [34,45]. These reductions in metal uptake by gel-immobilized microbial biomass have been projected to be due to diffusional limitations, or the masking of active sites on the biosorbent [34]. Moreover, part(s) of the cell surface might be shielded by the gel matrix and would thus not be available for metal binding [45]. In the present study, surface immobilization of *P. chrysosporium* (B1) on the structural fibrous network of papaya wood (B2) provides a direct contact of biomass to metal solution which is well suited for biosorption than the enclosed or beaded immobilization systems based on polymeric gel structures.

Table 1
Biosorption capacity of HB matrix produced in different batches

Cd(II) concentration (mg l^{-1})	Cd(II) removed (mg g^{-1} HB)					
	Batch 1	Batch 2	Batch 3	Mean	S.D.	R.S.D. (%)
50	47.85	50.14	48.60	48.86	1.17	2.39
100	89.24	86.93	88.05	88.07	1.15	1.30
200	128.63	125.37	124.89	126.29	2.03	1.61
300	140.36	136.85	137.52	138.24	1.86	1.34
400	141.15	138.79	142.28	140.74	1.78	1.26
500	143.81	141.63	141.81	141.63	2.27	1.60

The 100 mg of HB matrix was incubated in 100 ml Cd(II) solution (50–500 mg l^{-1}) at pH 5.0.

3.4. Adsorption isotherms

Analysis of equilibrium data is important for developing a prototype that can be used for design purposes. Several isotherm equations have been used for the equilibrium modelling of biosorption systems. Out of these isotherm equations, two were applied on the data obtained during this study, namely, the Freundlich and Langmuir isotherms. For each isotherm, initial Cd(II) concentrations were varied while the HB matrix weight in each sample was kept constant. The linearized Langmuir and Freundlich adsorption isotherms of Cd(II) ions obtained for HB matrix are given in Fig. 6a and b. The Langmuir and Freundlich adsorption constants evaluated from these isotherms with the correlation coefficients are presented in Table 3. Very high regression correlation coefficient (>0.991) was found for Langmuir isotherms than the Freundlich isotherms model, which

Table 2
Comparison between the cadmium (II) removal by HB and others immobilized and free biosorbents found in the literature

Biosorbents	Operational conditions				q_{eq} (mg g^{-1})	Reference
	pH	T (°C)	C_i (mg l^{-1})	M (g l^{-1})		
Fungus free biomass						
Aspergillus niger	4.0	26	75.0	2.0	17.40	[8]
Mucor rouxii	5.0	n.a.	10.0	0.66	8.46	[9]
Phanerochaete chrysosporium	6.0	25	5–500	4.0	23.4	[10]
Phomopsis sp.	6.0	n.a.	58.72	2.0	26	[11]
Polyporus versicolor	6.0	20	30–700	n.a	118.2	[12]
Rhizopus arrhizus	5–6	23	22–394	2.0	65.23	[13]
Fungal immobilized biomass						
Lentmus sajor-caju[ca]	6.0	25	200	1.0	123.5	[39]
Phanerochaete chrysosporium[ca]	6.0	30	200	0.11	75.1	[40]
Phanerochaete chrysosporium[ls]	6.0	25	10–500	1.0	85.98	[22]
Rhizopus oligosporus[puf]	5.3	30	300	1.0	34.25	[31]
Trametes versicolor[cmc]	6	20	700	n.a	153	[41]
Trametes versicolor[ca]	5.5	25	600	1.0	120.6	[42]
Agro-based plant waste materials						
Black gram husk	5.0	25	10–800	5.0	42.56	[17]
Fibrous network of papaya wood	5.0	25	5–500	5.0	17.35	[18]
Petiolar felt-sheath of palm	5.0	25	100	5.0	10.82	[19]
Commercial ion exchange resins						
Amberlite 200	4.8	n.a.	2249.6	5.0	202.46	[43]
Amberlite IRC-718	4.8	n.a.	2249.6	5.0	146.22	[43]
Doulite GT-73	4.8	n.a.	2249.6	5.0	55.12	[43]
Dowex 50 W	5.0	30	112.48	1.0	134.97	[44]
HB	6.0	25	50–500	1.0	141.63	[P.S.]

ca: Calcium algmate; ls: loofa sponge; puf: polyurethane foam, cmc: carboxyrnethylcellulose; P.S.: present study.

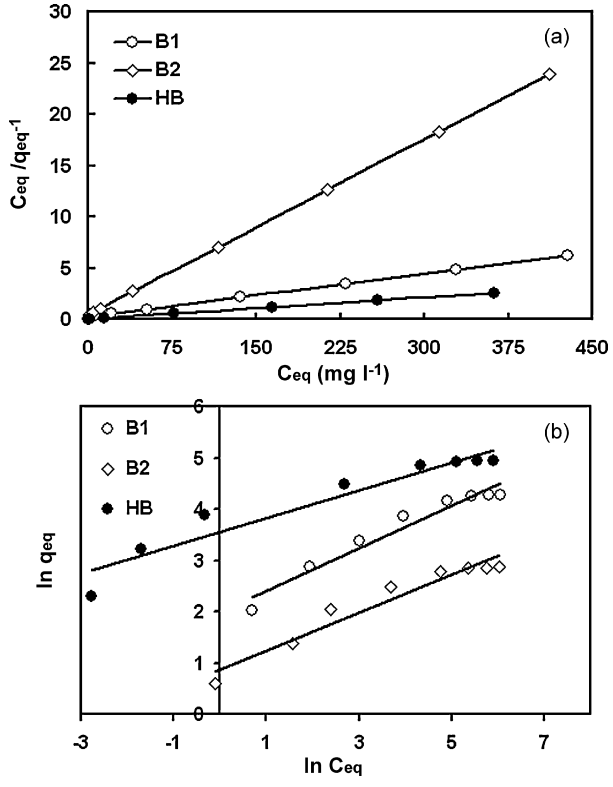

Fig. 6. The linearized (a) Langmuir and (b) Freundlich adsorption adsorption isotherms for the sorption of Cd(II) by *Phanerochaete chrysosporium* hyphal biomass (B1), fibrous network of papaya wood (B2) and hybrid biosorbent (HB) matrix.

suggests that the adsorption process by HB was better defined by Langmuir than by the Freundlich equation.

3.5. Biosorption kinetics modelling

In order to analyze the biosorption kinetics of Cd(II) ions, the pseudo-first order and the pseudo-second order kinetics models were applied to the data. The experimental data were observed to fit well to the pseudo-second order equation (Fig. 7a and b). The comparison of experimental biosorption capacities and the theoretical values calculated from the two kinetics equations are presented in Table 4. The theoretical q_{eq} values, estimated from the first order kinetics model, were significantly different than the experimental values, while the correlation coefficients were also found to be lower. These results indicate that the first order kinetics model does not describe the biosorption of Cd(II) by the HB matrix well. The correlation coefficients for the linear plots of t/q_t against t for the second order equation were observed to be close to 1 for the contact time of 60 min. The theoretical q_{eq} value for HB matrix was also very close to the experimental q_{eq} values in the case of second order kinetics (Table 4). These observations suggest that Cd(II) biosorption by HB matrix was not described by a the first order kinetics, while the pseudo-second order kinetics model, based on the assumption that the rate-limiting step may be the biosorption involving valence forces through sharing or exchange of electrons between biosorbent and sorbate, provides a good correlation of the data [29].

Table 3
Isotherms model constants and correlation coefficients for biosorption of Cd(II) ions from aqueous solution

Biosorbents	Langmuir isotherms model			Freundlich isotherms model		
	q_{max} (mg g^{-1})	b (l mg^{-1})	r^2	K_F	n	r^2
B1	68.61 ± 2.47	0.058	0.996	7.13	2.41	0.949
B2	17.24 ± 0.72	0.043	0.991	1.85	2.38	0.908
HB	141.32 ± 3.25	1.24	0.996	34.98	3.67	0.920

q_{max} is maximum Cd(II) uptake (mg g^{-1} biosorbent) and b is the equilibrium constant for Langmuir isotherm model, K_F and n are the Freundlich constants, r^2 is correlation coefficient.

Table 4
Theoretically determined constants of pseudo-first and second order reaction kinetics based on the sorption of metals from 100 mg l^{-1} Cd(II) solutions, pH 5, by 1 g l^{-1} B1 and HB matrix during shake flask metal-sorbent contact at 100 rpm for 120 min

Biosorbent	Experimental q_{eq} (mg g^{-1})	First order constants			Second order constants		
		q_{eq} (mg g^{-1})	K_{1ad} (min^{-1})	r^2	q_{eq} (mg g^{-1})	K_{2ad} (g mg^{-1} min^{-1})	r^2
B1	48.55 ± 1.89	69.45	−0.054	0.966	49.81	0.0006	0.995
HB	92.36 ± 2.78	83.37	−0.071	0.969	93.71	0.0014	0.998

3.6. Continuous removal of Cd(II) by HB matrix in fixed-bed column bioreactor

Breakthrough curves obtained for the metal-binding potential of HB in a continuous liquid flow system at different Cd(II) concentrations are presented in Fig. 8. The Cd(II) loading curves showed an excellent, clear zone (i.e. 100% removal) before the breakthrough point. Approximately 43.0, 22.5 and 10.5 l of 5, 10 and 20 mg l^{-1} Cd(II) solution, respectively, were treated completely before breakthrough occurred. In the loading stage, a total of 319.18, 303.82 and 298.66 mg of Cd(II) was accumulated in the column for the three columns, respectively, operated at 5, 10 and 20 mg l^{-1} Cd(II) solution. The total biosorption capacity of HB packed in columns was obtained by numerical integration of the whole breakthrough curve. Thus, the Cd(II) biosorption capacity of the HB in the column operation at various Cd(II) concentrations ranged between 142.90 and 145.74 mg of Cd(II) g^{-1} biosorbent, which agrees well with the maximum value of 141.63 mg of Cd(II) g^{-1} biosorbent obtained in batch shake flask experiments.

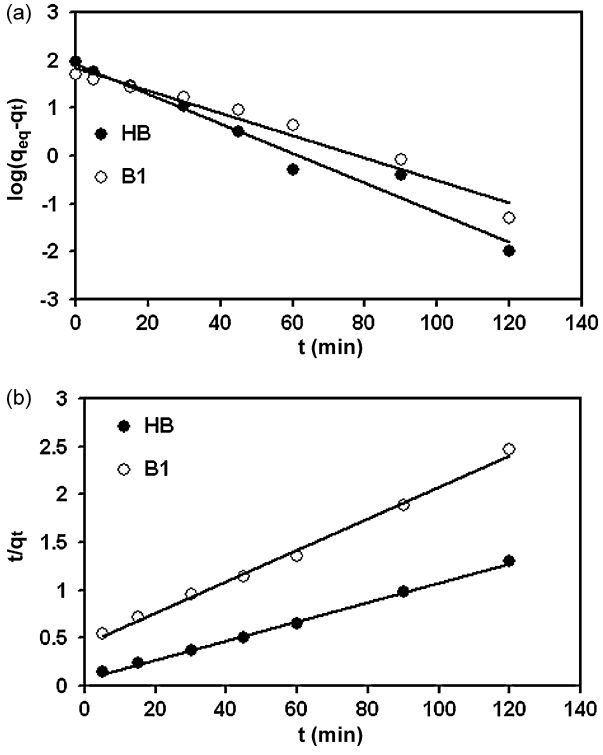

Fig. 7. Linearized pseudo-first and second order kinetic models for Cd(II) ions uptake by *Phanerochaete chrysosporium* hyphal biomass (B1), fibrous network of papaya wood (B2) and hybrid biosorbent (HB) matrix; Cd(II) concentration = 100 mg l^{-1}, concentration of biosorbents = 1.0 g l^{-1}, pH 5.0.

3.7. Desorption and reuse

Desorption of the adsorbed Cd(II) ions from HB matrix was studied in fixed-bed continuous flow columns using 0.05 M HCl. More than 98% of the adsorbed Cd(II) was desorbed from the Cd(II) loaded HB matrix (Fig. 9). The desorbent volume required to achieve the desirable 0.1 mg l^{-1} Cd(II) through the effluent discharged in columns operated with 5, 10 and 20 mg l^{-1}

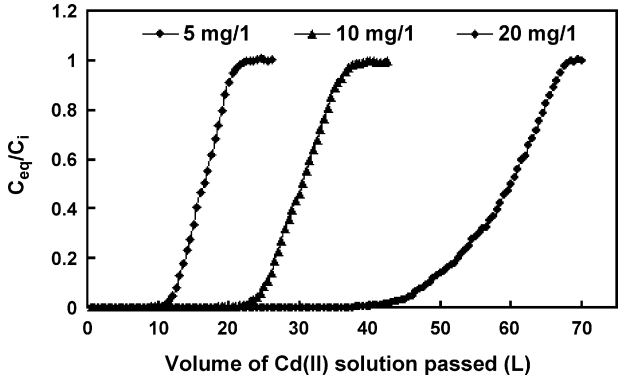

Fig. 8. Biosorption breakthrough curves for the removal of Cd(II) at different metal concentrations by hyphal biosorbent (HB) matrix in a fixed-bed column bioreactor.

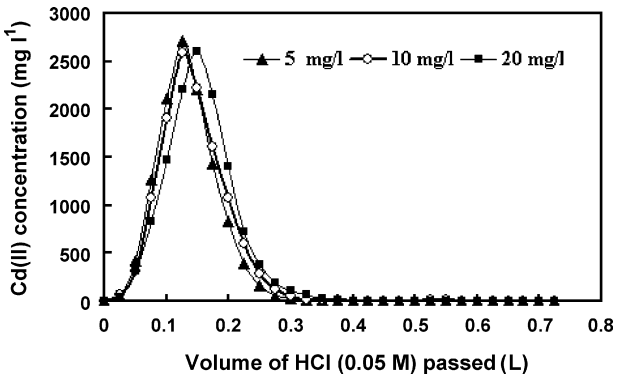

Fig. 9. Desorption breakthrough curves for the removal of Cd(II) by hybrid biosorbent (HB) matrix in a fixed-bed column bioreactor.

Cd(II), respectively, was 525, 475 and 500 ml. Compared with the wastewater treated volumes in the fixed-bed column bioreactor (43.0, 22.5 and 10.5 l of 5, 10, 20 mg Cd(II) l^{-1}, respectively), these volumes, respectively, represented the metal solution volume reduction of 130.5×, 81.05× and 44×. This is a major practical advantage, which results in a significant reduction in the volume of Cd(II) solution, for the final removal of metal ions from the effluent. In order to assess the reusability of the HB matrix, a series of adsorption–desorption experiments were performed. The HB matrix undergoing successive adsorption–desorption cycles retained good metal adsorption capacity even after five cycles. The total decrease in the sorption efficiency of HB matrix after five cycles was only about 2.68%, which shows that HB matrix has good potential to adsorb metal ions from aqueous solution and can be used repeatedly. Furthermore, no significant leakage of entrapped biomass or physical breakage of HB matrix was observed during five repeated adsorption–desorption cycles as was noted with other polymeric matrices used in immobilized systems [34,46], which ultimately resulted in the loss of biosorption capacity of these immobilized systems.

4. Conclusion

Efficient Cd(II) removing capacity of HB matrix observed during the present study and simplicity of the immobilization technique, used to entrap *P. chrysosporium* (B1) on to the papaya wood structural fibrous network (B2), to produce the HB matrix, indicate the of potential application of this novel and reusable metal biosorbent, which could be used as a significant tool for the development of a low-cost biomaterial-based polishing treatment of heavy metal wastes in industrial effluents. Since industrial effluents normally contain multimetal system, further studies to characterize the interaction of Cd(II) with HB in the presence of other metals or directly in diluted authentic wastewater are suggested.

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